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GENERAL MEETING OF DEPARTMENT OF CHEMICAL SCIENCES
OF ACADEMY OF SCIENCES USSR

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Two scientific papers were read at the general meeting of the Department of Chemical Sciences held on 25 and 26 June 1953.

A.I. Brodskiy, Corresponding Member of the Academy of Sciences USSR, and L.V. Sulima presented a paper entitled "The Isotope Exchange in Phosphorus Acids and the Tautomerism of Hypophosphorous Acid." They set forth the results of research on the isotopes of hydrogen and oxygen carried out in the Institute of Physical Chemistry imeni L.V. Pissarzhevskiy, Academy of Sciences USSR. This research was undertaken with the aim of substantiating the theory, advanced earlier, of retarded hydrogen exchange. The study clarified the problem of the existence of tautomerism in hypophosphorous and phosphorous acids and made the formulation of a number of laws of oxygen exchange possible.

It was determined that at room temperature, no hydrogen exchange takes place at P-H bonds of phosphorous acid and sodium hypophosphite. At 100° C, the exchange takes place very slowly (the half life equals 20 hours). In hypophosphorous acid, the exchange proceeds very rapidly already at 25° (the half life equals 16 minutes).

The results obtained confirm the theory that a X-H bonds the exchange with H^+ proceeds rapidly only when free electron pairs are present near the X atom. The usual forms of H_3PO_2 and H_3PO_3 with formally pentavalent phosphorous do not have these.

A rapid exchange in H_3PO_2 takes place with tautomeric form which has formally trivalent phosphorus and the constitution $\text{HP}(\text{OH})_2$. The investigation of the kinetics of the exchange showed that K equals 0.06 minutes⁻¹ for the speed of tautomeric conversion at 25°, which is in good agreement with data on the kinetics of the oxidation of H_3PO_2 (if it is assumed that the slow first phase of the latter is also a tautomeric conversion). Neither phosphorous acid nor the anions of either acids [H_3PO_2 or H_3PO_3] exhibit tautomerism. The absence of tautomerism in H_2PO_2^- is easily explained by the structure of this ion.

The tautomerism of hypophosphorous acid as proved by the investigation is the first experimentally substantiated example of tautomerism of an inorganic substance.

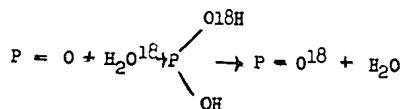
The investigation also showed that the isotopic exchange of oxygen proceeds rapidly in hypophosphorous acid at 40°, much more slowly in phosphorous acid at 100°, and not at all in orthophosphoric acid at 100°. In sodium hydrophosphite the exchange proceeds considerably slower and is not noticeable at all in phosphite (within 24 hours at 100°), as well as in the phosphates Na_3PO_4 , Na_2HPO_4 , and NaH_2PO_4 .

It is thus possible to draw the conclusion that the rate of exchange decreases with the increase in the number of oxygen atoms bound to the phosphorus atom. The rate of exchange is greater in the acids than in their anions.

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These regularities may be explained by the mechanism of exchange via an intermediate formation of a hydrated orthoform:



A comparison of data from the literature shows analogous regularities for the exchange at the bonds $C=O$, $N=O$ and $S=O$ of the corresponding acids and their salts.

The mechanism of exchange as described in the paper apparently constitutes one of the most frequent ones for the oxygen exchange in anorganic oxyanions, ketones and carboxylic acids.

The paper V.N. Tsvetkov, Doctor of Physicomathematical Sciences, was devoted to the problem of the mobility and shape of macromolecules in solution.

As is known, one of the characteristics of the structure of a polymer is the shape which the macromolecules assume in solution. Quantitatively it may be described with the aid of the mean square radius of the molecule which is an essential value in the determination of the degree of branching of the molecule chain. Experimentally the mean square radius of a macromolecule may be determined on the basis of measurements of the diffusion of light by the polymer solution as well as of the rate of transitional and rotary diffusion by macromolecules in solutions.

By applying an interference method to the measurement of the coefficient of transitional diffusion by the polymer in solution, V.N. Tsvetkov determined that the diffusion coefficient depends on two parameters, i.e. the hydrodynamic and the statistical; also that its value, which characterizes the properties of an individual molecule may be found only at sufficiently great dilutions of the solution.

As was pointed out in the paper, the rotatory diffusion coefficients of macromolecules may be defined by measuring the values and orientations of dynamic double light refraction in polymer solutions. To carry out the necessary experiments, V.N. Tsvetkov designed a special type of instrument, a dynamooptometer with an external rotor.

The study of polystyrene and polymethylene methacrylate fractions by the method indicated above disclosed that these polymers belong to the linear type.

The comparison of data obtained by the speaker by the methods of light diffusion, viscosity measurement and diffusion and dynamic double refraction permits drawing the conclusion that for a complete determination of the size and shape of macromolecules in solution it is necessary to take into account the degree of geometrical asymmetry of the bundle formed by the molecule in addition to considering the mean square radius.

At the second meeting, Academician N.N. Semenov's report on the results of the discussion of the report "The State of the Theory of Chemical Structure in Organic Chemistry" was read.

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